

Radiocarbon

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MASS-SPECTROMETER ANALYSES OF RADIOCARBON STANDARDS

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Twenty-four samples of CO₂ from combustion of the NBS oxalic-acid radiocarbon standard, submitted from 13 radiocarbon laboratories, were analyzed for C¹³ content in this laboratory in order to provide comparative data for normalizing the counting results. The samples were analyzed on Samson, a 60° sector, six-inch radius, McKinney-Nier type mass-spectrometer with magnetic switching between sample and standard gas feed to the instrument.

The CO₂ samples were received in sealed breakoffski flasks containing on the order of 100 cc of gas, except for the Lamont, Yale, Isotopes Inc., and La Jolla samples which were in sample tubes with stopcocks. Aliquots of 10-15 cc were taken for analysis by direct expansion of the gas into an evacuated gas pipette on a vacuum line. The Lamont, Isotopes Inc., and Socony Mobil samples contained small amounts of an impurity not condensable in liquid N₂, and the wet combustion sample from the National Physical Laboratory contained some water; these samples were purified with liquid N₂ and dry-ice traps. The other samples contained no detectable impurities.

The samples were analyzed in series against a single gas standard which had previously been well calibrated against the PDB Chicago C¹³ standard. The following corrections were applied to the raw δC^{13} values:

- a. Valve mixing: $f = 1.006$
- b. Fraction of mass 44 tail falling on mass 45: $f = 1.0066$
- c. CO₂ background in source: $f = 1.0033$
- d. O¹⁷ content of standard and sample gas: correction as given by Craig (1957).

The raw δC^{13} values are multiplied by the indicated factors; samples were also analyzed for O¹⁸ to obtain the corrections for O¹⁷ in the individual samples. The instrumental corrections were minimized for inter-comparison of standards with each other by using a spectrometer gas standard chosen to have a C¹³ content close to the oxalic-acid value (-24.8‰ relative to PDB). The mass-spectrometer has been shown to be exactly linear (to 0.1‰) over a range of 0 to -50‰.

Table 1 presents the results in terms of C¹³ enrichment relative to the Chicago PDB standard ($\delta^{13}C$), and also as enrichments ($\delta_w C^{13}$) relative to

TABLE 1

Isotopic composition of CO₂ from NBS oxalic-acid-radiocarbon standards. All samples represent the CO₂ which was actually counted except for La Jolla and Socony Mobil who do not use CO₂ as counter gas.

Laboratory ¹	$\delta^{13}\text{C}$	$\delta_{\text{w}}\text{C}^{13}$	$\delta^{18}\text{O}$	Oxalic Acid Combustion
Copenhagen				
K-301	-19.41	+5.73	-15.09	direct
K-302	-19.73	+5.40	-15.92	direct
K-303	-19.72	+5.42	—	—
K-303	-19.51	+5.63	-11.67	wet
Groningen				
1st series	-18.77	+6.39	-12.42	direct
Duplicate sample	-18.73	+6.43	-12.44	—
2nd series	-19.24	+5.91	-13.82	direct
Duplicate sample	-19.21	+5.94	-13.82	—
Isotopes, Inc.	-21.57	+3.52	-12.68	wet
La Jolla ²				
170 A	-31.34	-6.50	-2.75	wet
170 B	-31.37	-6.53	—	—
145	-22.72	+2.34	(-5.3)	direct
197	-21.84	+3.24	(-5.3)	wet
Lamont				
L-456 D	-19.05	+6.10	-11.60	wet
National Physical Lab.				
A	-18.94	+6.21	-10.86	wet
B	-21.43	+3.66	-12.63	direct
New Zealand				
CR-929	-19.50	+5.64	-10.20	direct
Duplicate sample	-19.45	+5.69	-10.35	—
Pennsylvania				
P-263	-25.67	-0.67	-16.29	wet
P-263	-25.70	-0.71	-16.36	—
Socony Mobil ³	-19.28	+5.87	-16.30	direct
Stockholm				
ST 532	-17.15	+8.05	-17.26	direct
Duplicate sample	-17.26	+7.94	-17.28	—
Trondheim				
T-200	-18.37	+6.80	-19.35	wet
Uppsala				
Oxalic acid-1	-18.97	+6.18	-13.24	direct
Yale	-20.01	+5.12	-12.22	wet

NOTES

¹ All sample numbers or letters denote separate combustions. "Duplicate sample" means duplicate flasks of gas from one combustion were received and analyzed. An analysis with no notation is a repeat analysis of the same gas, made as a check after the series was analyzed (K-302 and P-263).

² The samples are CO₂ from recombination of the C₂H₂ which was actually counted. The C₂H₂ samples were combusted with CuO and O₂ in a closed recycling system as described by Craig (1953), which prevents fractionation in this step. Samples 170A and 170B are duplicate recombinations of the same C₂H₂ from a single combustion. (The O¹⁸ value—5.3 is the average of several other combustions, as the last two samples were not analyzed for oxygen.)

³ The sample represents CO₂ produced from the combustion of oxalic acid. The CO₂ was then hydrogenated to CH₄ for counting; the isotopic analysis does not include any fractionation which may occur in the preparation of the CH₄.

the C^{13} content of average wood which is taken as $\delta = -25\text{‰}$ relative to PDB (Craig, 1953). The delta values are defined by:

$$\delta^r = 1000 [(R/R_{\text{PDB}}) - 1]; \delta_w = 1000 [(R/R_{\text{wood}}) - 1]$$

where $R = C^{13}/C^{12}$, and $R_{\text{wood}} \equiv 0.975 R_{\text{PDB}}$. The absolute values of the ratios are given by Craig (1957). The uncertainty in the δ values is $\pm 0.1\text{‰}$.

Table 1 also shows the measured O^{18}/O^{16} enrichments in per mil ($\delta^{18}O$) relative to PDB standard CO_2 , as it may be of some interest to record the range and variation of O^{18} content in the different combustions. The observed data are quite typical of values observed for carbon combustion with CuO and tank O_2 (Craig, 1957, p. 141) except for the C_2H_2 combustions which were done with CuO and tank O_2 and deviate for an unknown reason.

Average values for both "direct" combustion (with O_2) and wet combustion were computed by using only one value for direct or wet combustion for each laboratory; when duplicates or samples from more than one combustion of the same type were analyzed the average of these was used as one analysis. In order to compare combustions directly, the La Jolla data were not included, as these values include the effect of the additional step of making C_2H_2 from the CO_2 obtained from the combustion.

The average direct combustion value thus obtained (7 laboratories) is $\delta^{13}C = -19.3\text{‰}$. The average wet combustion value (excluding also the Pennsylvania value which seems clearly divergent; 6 laboratories) is -19.6‰ , indicating that wet oxidation is probably about as reliable as direct combustion with O_2 , at least for oxalic acid. A histogram of all the data appears markedly non-Gaussian, with a pronounced tendency for enrichment of C^{12} in the product CO_2 , as might be expected if some combustions are less complete than others.

δC^{14} values relative to any standard are given by:

$$\delta_{14} = 2\delta_{13} + 10^{-3}\delta_{13}^2 \quad (\delta \text{ values in per mil})$$

assuming that for any separation process $\alpha_{14} = \alpha_{13}^2$ (Craig, 1954, p. 133). The total C^{13} range, excluding the one very light La Jolla wet combustion value and the Pennsylvania value, is 5.5‰ , indicating that the probable spread among various laboratories for careful work will be of the order of only 1% variation in reported activity when fractionation is neglected, in the case of a single sample. The range of C^{13} variation in ancient and modern wood is of the order of 10‰ (Craig, 1953) and is thus a more important factor than most of the laboratory effects observed in the present study.

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